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(21) International Application Number: PCT/EP99/02721 (22) International Filing Date: 22 April 1999 (22.04.99) (30) Priority Data: 98107493.3 24 April 1998 (24.04.98) EP (71) Applicant (for all designated States except US): FINA RESEARCH S.A. [BE/BE]; Zone Industrielle C, B-7181 Seneffe (BE). (72) Inventor; and (75) Inventor/Applicant (for US only): DEBRAS, Guy [BE/BE]; Rue Champ de la Chapelle 12, B-6210 Frasnes-lez-Gosselies (BE). (74) Common Representative: FINA RESEARCH S.A.; Patent Dept., Zone Industrielle C, B-7181 Seneffe (BE).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PRODUCTION OF POLYETHYLENE HAVING IMPROVED MECHANICAL PROPERTIES		
(57) Abstract A process for producing a polyethylene resin having improved mechanical properties, the process comprising polymerising ethylene in the presence of a chromium-based catalyst to make polyethylene homopolymer in a first polymerisation reactor and in a second polymerization reactor downstream of the first polymerisation reactor copolymerising ethylene in the presence of the chromium-based catalyst and a co-catalyst from ethylene monomer and comonomer generated in-situ in the second polymerisation reactor to make polyethylene copolymer.		

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PRODUCTION OF POLYETHYLENE HAVING
IMPROVED MECHANICAL PROPERTIES

The present invention relates to a process for producing polyethylene, in particular high density polyethylene having improved mechanical properties.

Polyethylene is known for use in the manufacture of a wide variety of articles. The polyethylene polymerisation process can be varied in a number of respects to product a wide variety of resultant polyethylene resins having different physical properties which render the various resins suitable for use in different applications. In particular, it is known to use polyethylene for use in applications where the polyethylene is required to have crack resistance, both resistance to rapid and to slow crack growth. For example, polyethylene is known for use in the manufacture of pipes where it is required that the material of the pipe has sufficient crack resistance so as to avoid inadvertent fracture in service. Polyethylene is also known for use in the manufacture of blow moulded articles where a high environmental stress cracking resistance (ESCR) is required.

Chromium-based catalysts used for the production of polyethylene have been known for some time. It is known in the art that the physical properties, in particular the mechanical properties, of a polyethylene product can vary depending on what catalytic system was employed to make the polyethylene. This is because different catalyst systems tend to yield different molecular weight distributions in the polyethylene produced.

It is further known in the art that the mechanical properties of a polyethylene resin, for example the ESCR for blow moulding resins, the impact resistance for film forming resins, and slow crack growth resistance for pipe forming resins, tend

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to be better when the high molecular weight fraction of the polyethylene is copolymerised.

US-A-5208309 discloses the manufacture of linear very low density polyethylene in which a copolymer of ethylene and a higher alpha-olefin is produced using an activated and subsequently carbon monoxide reduced chromium containing catalyst system and an alkyl aluminium or alkyl boron co-catalyst. The specification states that in the process disclosed therein, it is believed that additional comonomers, i.e. in addition to those added to the polymerisation reactor, can be generated in-situ in the polymerisation reactor or in the reaction zone. Such comonomer is incorporated into the copolymer.

EP-A-0307907 discloses a process for olefin polymerisation in which in-situ comonomer production is employed using a carbon monoxide reduced polymerisation catalyst system. The addition of hydrogen to the reactor enables the regulation and control of the characteristics of the resultant polymer.

The processes disclosed in those two patent specifications suffer from the disadvantage that apart from the density of the resultant polyethylene being low, around 0.890 to 0.915g/cc for US-A-5208309 and around 0.93 to 0.94g/cc for EP-A-0307907, the resultant polymer does not have particular broad molecular weight distribution or a particularly high shear response (SR), the shear response being the ratio of the high load melt index (HLMI) and the melt index (MI_2).

EP-A-0832905 discloses a process for preparing polyethylene having a large molecular weight distribution employing two reactors in series and in which a polyethylene homopolymer is produced in the first reactor and a polyethylene copolymer with 1-hexene is produced in the second reactor by the addition of 1-hexene into the second reactor.

EP-A-0739909 discloses the production of ethylene polymers

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using, for example, a single reactor having two separated stages simulating two reactors in series. The first polymer is a copolymer of ethylene with hexene and the second polymer is produced by additionally adding hydrogen into the reactor.

The present invention aims in one aspect to provide a process for producing polyethylene having improved mechanical properties.

Accordingly, the present invention provides a process for producing a polyethylene resin having improved mechanical properties, the process comprising polymerising ethylene in the presence of a chromium-based catalyst to make polyethylene homopolymer in a first polymerisation reactor and in a second polymerisation reactor downstream of the first polymerisation reactor copolymerising ethylene in the presence of the chromium-based catalyst and a co-catalyst from ethylene monomer and comonomer generated in-situ in the second polymerisation reactor to make polyethylene copolymer.

As a result of the in-situ generation of comonomer, no comonomer is introduced into the second reactor. This avoids the need for a comonomer feed to the reactor system.

Preferably, the chromium-based catalyst has been chemically reduced, for example by carbon monoxide, prior to the introduction thereof into the first polymerisation reactor. More preferably, the chromium-based catalyst additionally contains titanium.

The present invention is predicated on the surprising discovery by the present inventors that the use of a two-stage polymerisation process using a chromium-based catalyst, wherein only ethylene is introduced as a monomer and the catalyst systems present in the first and second stages are controlled so as to produce in the first stage a homopolymer and the in the second stage a copolymer in which comonomer generated in-situ in the

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second stage is incorporated into the copolymer, can in turn yield a broader molecular weight distribution and a higher shear response for the resultant polyethylene resin, in turn yielding improved mechanical properties for the resin.

The chromium-based catalyst preferably comprises a supported chromium oxide catalyst having a titania-containing support, for example a composite silica and titania support. A particularly preferred chromium-based catalyst may comprise from 0.5 to 5 wt% chromium, preferably around 1 wt% chromium, such as 0.9 wt% chromium based on the weight of the chromium-based catalyst. The support comprises from 1 to 5wt% titanium, preferably at least 2 wt% titanium, more preferably around 2 to 3 wt% titanium, yet more preferably around 2.3 wt% titanium based on the weight of the chromium-based catalyst. The chromium-based catalyst may have a specific surface area of from 200 to 700 m²/g, preferably from 400 to 550 m²/g and a volume porosity of greater than 2 cc/g preferably from 2 to 3 cc/g.

A particularly preferred chromium-based catalyst ("catalyst 1") for use in the present invention has an average pore radius of 190A, a pore volume of around 2.1 cc/g, a specific surface area of around 510 m²/g and a chromium content of around 0.9 wt% based on the weight of the chromium-containing catalyst. The support comprises a composite silica and titania support. The amount of titania in the support provides that the catalyst as a whole comprises around 2.3 wt% titanium.

The catalyst may be subjected to an initial activation step in air at an elevated activation temperature. The activation temperature preferably ranges from 500 to 850°C, more preferably around 700 to 800°C.

The chromium-based catalyst is preferably subjected to a chemical reduction process in which at least a portion of the chromium is reduced to a low valence state. Preferably, the chromium-based catalyst is reduced in an atmosphere of dry carbon

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monoxide in nitrogen gas, typically 8% CO in N₂ at a temperature of from 250 to 500°C, more preferably around 340°C, for a period typically around 30 minutes.

In the preferred polymerisation process of the present invention, the homopolymerisation and copolymerisation processes are carried out in the liquid phase, the liquid comprising ethylene in an inert diluent. The inert diluent is preferably isobutane. The homopolymerisation or copolymerisation process is typically carried out at a temperature of from 80 to 110°C, more preferably from 90 to 100°C, and at a pressure of from 20 to 42 bars, more preferably at a minimum pressure of around 24 bars. The temperature is selected so as to obtain a particular molecular weight distribution in each of the homo- and co-polymers produced in the first and second reactors respectively.

Typically, in the homopolymerisation and copolymerisation processes, the ethylene monomer comprises from 0.5 to 8% by weight, typically around 6% by weight, of the total weight of the ethylene in the inert diluent. Since the comonomer is generated in-situ in the second reactor, no comonomer is fed to the second reactor. All of the comonomer copolymerised with ethylene in the second reactor is generated in-situ in the second reactor.

In the first stage of the polymerisation process the chromium-based catalyst is used alone in the absence of a co-catalyst. In the second stage of the polymerisation process a co-catalyst comprising at least one metal alkyl and/or at least one alkyl metal oxane is introduced together with further ethylene monomer. The metal alkyl preferably comprises triethyl boron (TEB), triethyl aluminium (TEA), dibutyl magnesium (MgBu₂), diethyl zinc (DEZ) or butyl lithium (BuLi). The alkyl metal oxane preferably comprises diethyl aluminium ethoxy (DEALE) or methyl aluminium oxane (MAO). Preferably, the co-catalyst is introduced into the second polymerisation reactor in an amount of at least 1ppm, more preferably from 2 to 10ppm, based on the weight of the inert diluent. The amount of co-catalyst employed

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is selected so as to provide in the copolymer produced in the second polymerisation reactor a selected density for the copolymer.

In accordance with the process of the invention, the chromium-based catalyst, preferably having being reduced by carbon monoxide, is introduced into a first polymerisation reactor together with ethylene monomer. The ethylene homopolymerises to form polyethylene and typically the resultant polyethylene, if discharged from the first polymerisation reactor, has an HLMI of from around 24 to around 31g/10min (the HLMI being measured using the procedures of ASTM D 1238 using a load of 21.6kg at 190°C), and a density of at least around 0.96g/cc. The homopolymer produced in the first reactor comprises the relatively high density, relatively low molecular weight, fraction of the resultant polyethylene resin.

The product from the first polymerisation reactor is then fed into the downstream second polymerisation reactor and the metal alkyl and additional ethylene are introduced into the second polymerisation reactor. The provision of the co-catalyst of at least one metal alkyl and/or at least one alkyl metal oxane causes in-situ generation of comonomer from the ethylene whereby such comonomer is introduced into the polyethylene resin including both homopolymer and copolymer to form a polyethylene copolymer. As for the first reactor, the polymerisation temperature in the second reactor can be selected for targeting a particular molecular weight distribution in the resultant polyethylene resin. The resultant polyethylene resin including both homopolymer and copolymer is discharged from the second reactor and then separated from the diluent which can be recycled. The resultant polyethylene resin typically comprises from 40 to 60wt% homopolymer produced in the first reactor and from 60 to 40wt% copolymer produced in the second reactor. A most typical polyethylene resin comprises equal amounts by weight of the homopolymer and the copolymer.

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The resultant polyethylene resin tends to have a lower density and a lower HLMI than the homopolymer produced in the first polymerisation reactor. This is because in the second polymerisation reactor, as a result of the in-situ generation of comonomer, a copolymer is produced which tends to have a relatively high molecular weight and a relatively low density as compared to the homopolymer produced in the first polymerisation reactor. This yields in turn for the composite polyethylene resin a broad molecular weight distribution and a high shear response, providing improved mechanical properties for the resin. Typically, in the resultant polyethylene resin the density is around 0.95g/cc, most typically ranging from around 0.945 to around 0.955g/cc, and an HLMI ranging from around 5 to around 40g/10min.

The process of the invention can provide polyethylene resins having improved mechanical properties. The homopolymer produced in the first polymerisation reactor has a relatively low molecular weight and the copolymer produced in the second polymerisation reactor has a relatively high molecular weight, the amount of comonomer which has been generated in-situ in the second reactor and has been introduced into the copolymer tending to have a distribution thereof in the copolymer which decreases at increasing molecular weight. When the two resin fractions are mixed together in the resultant polyethylene resin, the two molecular weight distributions overlap, thereby yielding in the resultant polyethylene resin a broad molecular weight distribution and a high shear response. This in turn provides improved mechanical properties, such as environmental stress crack resistance, impact resistance and slow crack growth resistance.

The present invention will now be described with reference to the following non-limiting Examples.

EXAMPLES 1 TO 7

In these examples, a polyethylene resin was produced by the polymerisation process of the present invention, in which a two-stage polymerisation process was employed with two serially-connected polymerisation reactors. In the first reactor, ethylene in isobutane as an inert diluent was introduced into the reactor together with the chromium-based catalyst identified as catalyst 1 above which had been activated in dry air at a temperature of around 800°C and had been subjected to carbon monoxide reduction at a temperature of around 340°C for a period of around 30 minutes in an atmosphere comprising 8% CO in nitrogen gas. The catalyst had a pore volume of 2.1cc/g and a specific surface area of 510m²/g. The catalyst comprised 0.9% Cr and 2.3% Ti, each based on the weight of the catalyst. The ethylene was present in the isobutane as an inert diluent in an amount of around 4wt%. The polymerisation temperature was around 95°C and the polymerisation pressure was around 30 bars. These Examples were performed at this pressure on bench-scale reactors. In liquid-full reactors, typically used in commercial production, the pressure would be around 40 bars. In the first polymerisation reactor, a polyethylene homopolymer was formed which was then fed as polyethylene fluff to the second serially connected reactor downstream of the first reactor. The chromium-based catalyst was also conveyed to the second reactor and an additional metal alkyl or alkyl metal oxane co-catalyst was introduced into the second reactor, together with additional ethylene monomer. In the second polymerisation reactor, the ethylene comprised around 6wt% ethylene in the isobutane inert diluent. The reaction temperature was around 95°C, as for the first reactor, and the pressure was slightly lower than that for the first reactor to provide throughput of the reactants and the catalyst from the first reactor to the second reactor. Table 1 shows the type of co-catalyst introduced into the second reactor in each of Examples 1 to 7, together with the amount of such co-catalyst.

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Table 1 also shows the properties, namely the HLMI and the density, of the polyethylene homopolymer produced in the first reactor in each of Examples 1 to 7, together with the properties, namely the HLMI and the density, of the resultant polyethylene resin produced following production of the polyethylene copolymer in the second reactor. For each Example, the polyethylene homopolymer produced in the first reactor comprised around 50wt% of the resultant polyethylene resin.

EXAMPLE 8

In this Example, the chromium-based catalyst comprised the same catalyst as in Examples 1 to 7, but the catalyst had not been subjected to a preliminary carbon monoxide reduction step and had been activated at a lower temperature of 720°C. The polymerisation process was otherwise performed in the same manner as for Examples 1 to 7. In the first reactor, the temperature was around 106°C and the properties of the resultant polyethylene and the polymer are specified in Table 2. The polyethylene homopolymer comprised 50wt% of the resultant polyethylene resin. In the second reactor, the temperature was reduced to around 80°C and 10ppm TEB were introduced into the reactor. The properties of the resultant polyethylene resin are specified in Table 2.

It may be seen from Table 2 that the use of a chromium-based catalyst which had not been subjected to carbon monoxide reduction yielded on the one hand a greater HLMI and on the other hand a lower density for the resultant polyethylene resin than for Examples 1 to 7. This indicates that the polyethylene homopolymer had a relatively low molecular weight distribution. For the resultant polyethylene resin following the production of the polyethylene copolymer in the second reactor, it may be seen that the HLMI value is particularly low, this indicating a high molecular weight for the polyethylene copolymer, and in turn indicating low formation of the in-situ comonomer in the second reactor.

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TABLE 1

REACTOR 1	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
<u>PRODUCT</u>							
HLMI (g/10')	30.6	28.2	30.8	26.2	31.4	24.7	25.8
density (g/cc)	.9639	.9634	.964	.963	.9642	.9637	.9639
wt%	50	50	50	50	50	50	50
REACTOR 2							
<u>METAL ALKYL OR ALKYL METAL OXANE CO-CATALYST</u>	TEB	TEB	TEB	DEALE	DEALE	TEA	TEA
type	2	4	8	4	8	4	8
ppm							
<u>PRODUCT</u>							
HLMI (g/10')	18.2	30.4	39.7	15.8	28.7	9.9	11.8
density (g/cc)	.9540	.9496	.9458	.9527	.9495	0.9545	.9532

TABLE 2

REACTOR 1	EXAMPLE 8
T (°C)	106
HLMI (g/10')	60
density (g/cc)	.964
wt%	50
REACTOR 2	
T (°C)	80
TEB (ppm)	10
HLMI (g/10')	7.28
MI ₂ (g/10')	0.028
density (g/cc)	.9503
SR	280

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CLAIMS:

1. A process for producing a polyethylene resin having improved mechanical properties, the process comprising polymerising ethylene in the presence of a chromium-based catalyst to make polyethylene homopolymer in a first polymerisation reactor and in a second polymerisation reactor downstream of the first polymerisation reactor copolymerising ethylene in the presence of the chromium-based catalyst and a co-catalyst from ethylene monomer and comonomer generated in-situ in the second polymerisation reactor to make polyethylene copolymer.
2. A process according to claim 1 wherein the chromium-based catalyst has been chemically reduced prior to the introduction thereof into the first polymerisation reactor.
3. A process according to claim 2 wherein the chromium-based catalyst has been chemically reduced by carbon monoxide.
4. A process according to any foregoing claim wherein the chromium-based catalyst has a titania-containing support.
5. A process according to any foregoing claim wherein the chromium-based catalyst comprises around 1wt% chromium and from 1 to 5wt% titanium, each based on the weight of the chromium-based catalyst.
6. A process according to claim 5 wherein the chromium-based catalyst comprises from 2 to 3wt% titanium, based on the weight of the chromium-based catalyst.
7. A process according to any foregoing claim wherein the co-catalyst is selected from at least one of a metal alkyl and an alkyl metal oxane.
8. A process according to claim 7 wherein the co-catalyst comprises at least one metal alkyl selected from at least one of

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triethyl boron, triethyl aluminium, dibutyl magnesium, diethyl zinc and butyl lithium.

9. A process according to claim 7 wherein the alkyl metal oxane is selected from at least one of diethylene aluminium ethoxy and methyl aluminium oxane.

10. A process according to any one of claims 7 to 9 wherein the co-catalyst is present in an amount of from 2 to 10ppm based on the weight of an inert diluent for the ethylene monomer in the polymerisation reactors.

11. A process according to any foregoing claim wherein the polyethylene homopolymer comprises from 40 to 60wt% of the polyethylene resin.

12. A process according to any foregoing claim wherein the polyethylene resin has an HLMI of from 5 to 40g/10min.

13. A process according to any foregoing claim wherein the polyethylene resin has a density of from 0.945 to 0.955g/cc.

14. A process according to any foregoing claim wherein the homopolymer produced in the first polymerisation reactor has a density of at least around 0.96g/cc.

INTERNATIONAL SEARCH REPORT

National Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F210/02 C08F2/00 C08F4/69

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 832 905 A (FINA RESEARCH) 1 April 1998 (1998-04-01) cited in the application abstract claims 1-3,6,10,11 page 3, line 30 - line 35 examples 1,2	1,4,5, 7-9,11, 12,14
A		2,3
A		10,13
X	EP 0 739 909 A (SOLVAY) 30 October 1996 (1996-10-30) cited in the application example 7 claims 1,11,13	1,7,8
A	column 8, line 25 - column 10, line 36 --- -/--	4-6

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/02721

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category ²	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 307 907 A (PHILLIPS PETROLEUM CO) 22 March 1989 (1989-03-22) cited in the application claims 1,2,5,6,8 page 2, line 31 - line 32 page 3, line 19 - line 21 page 5, line 38 - line 45 * example 1 (run 101) and example III (run 301 and 306)</p> <p style="text-align: center;">-----</p>	<p>1-9,12, 13</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/02721

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0832905 A	01-04-1998	EP 0829495 A	18-03-1998
EP 0739909 A	30-10-1996	BE 1009308 A	04-02-1997
		AU 697264 B	01-10-1998
		AU 5069896 A	07-11-1996
		BR 9602100 A	06-10-1998
		CA 2174400 A	29-10-1996
		CN 1147521 A	16-04-1997
		CZ 9601222 A	13-11-1996
		EP 0908474 A	14-04-1999
		EP 0906922 A	07-04-1999
		HU 9601108 A	29-12-1997
		JP 8301932 A	19-11-1996
		NO 961697 A	29-10-1996
		ZA 9603067 A	29-07-1996
EP 0307907 A	22-03-1989	AT 85800 T	15-03-1993
		AU 2178388 A	23-03-1989
		CA 1309801 A	03-11-1992
		CN 1032016 A, B	29-03-1989
		DE 3878515 A	25-03-1993
		ES 2053661 T	01-08-1994
		GR 3007277 T	30-07-1993
		HU 209315 B	28-04-1994
		IN 170952 A	20-06-1992
		JP 1104603 A	21-04-1989
		JP 1985741 C	25-10-1995
		JP 7017707 B	01-03-1995
		KR 9404125 B	13-05-1994
		PH 25468 A	01-07-1991